

THE ACTION OF LIGHT
ON SOME ORGANIC ACIDS IN THE PRESENCE
OF URANIUM SALTS.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

HENRY FAY.

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CONTENTS.

Historical.....	5
Work of H. C. Jones.....	9
Decomposition of Oxalic Acid.....	11
Decomposition of Uranyl Oxalate.....	13
Products of Decomposition.....	13
Formation of Formic Acid in decomposition of Oxalic Acid.....	16
Decomposition of Malonic Acid.....	17
Decomposition of Succinic Acid.....	18
Decomposition of Tartaric Acid.....	19
Decomposition of Isobutyric Acid.....	20
Decomposition of Propionic Acid.....	22
Decomposition of Acetic Acid.....	22
Comparison of rates of decomposition.....	23
Summary	25
Biographical	26

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THE ACTION OF LIGHT ON SOME ORGANIC ACIDS IN THE PRESENCE OF URANIUM SALTS.

HISTORICAL.

The early history of photo-chemical reactions is involved with the history of photography. Shulze in 1727 proved experimentally that the darkening of silver salts was due to the action of light, and in 1799 Sheele¹ showed the effects of different parts of the spectrum. It had been noticed several centuries before that silver salts were subject to change, but the work of Shulze was the first conclusive evidence that this change was due to the action of light. In the early part of this century the action of light on plant growth was studied by many investigators who received the incentive from a suggestion made by Priestley.

Certain physical phenomena were early noticed as the effect on crystallization by Petit,² who showed, in 1722, that solutions of potassium nitrate and ammonium chloride crystallize more readily in the sunlight than in the dark. These effects were studied more fully by Chaptal³ and Dize⁴. In 1848 Becquerel⁵ published his excellent researches on the phosphorescence of the sulphides of barium, calcium, and strontium, but none of these researches threw any light on the chemistry of the reactions caused by sunlight. Photography was being developed in the early part of the century and various effects were noticed, but the chemistry involved was not worked out. During this period many inorganic salts were found to undergo some change when exposed to the sunlight and in general this change was a reduction, especially if there was an oxidizable organic substance present.

Among the salts most extensively studied were the salts of uranium. Before taking up the study of the reactions involved when uranium salts are decomposed in the sunlight, it would be well to review the work which has been done on

¹ *Traité de l' Air et de Feu.*

² *Mém. de Paris, 1722.*

³ *Jour. de. Phys., vol. 34.*

⁴ *Sur la cristallisation, etc., 1789.*

⁵ *Ann. Chim. Phys. [3], 9, 257.*

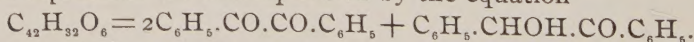
the organic substances which are subject to change when exposed to the light. Many observations have been recorded in which the fact is simply stated that certain substances are sensitive to light, but only in a few cases has the reaction been a clear one. In the cases studied the reactions can be classified under one of these three classes—substitution, direct combination, and polymerization.

Dumas¹ has shown that the hydrogen atoms of the methyl group in acetic acid can be replaced by chlorine when the two substances are brought together in the direct sunlight, forming a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm² who has shown that when aromatic hydrocarbons having a side chain were treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second class come the researches of Cahours,³ who prepared perchloromethyl oxalate and formate by bringing together the acids and alcohol in presence of chlorine. When exposed to the sunlight the reaction takes place forming the etherial salts.

Chastaing⁴ exposed acetic and butyric acids with alcohol and by means of titration was able to measure the rate of etherification.

Somewhat similar are the facts discovered by Klinger,⁵ who showed that aldehydes have the power of combining with phenanthrenequinone. He also noticed that if a reducible substance be exposed to light in presence of an oxidizable one, the solvent is oxidized while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone and at the same time the solvent, ether, was oxidized to acetic aldehyde. He found that benzil in ether solution passed over into a substance which he called benzil-benzöin on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation



¹ Ann. Chim. Phys. [2], **73**, 77.

² Ber. d. chem. Ges., **18**, 350, 606, 1272; **19**, 212.

³ Comp. Rend., **23**, 1070.

⁴ Ann. Chim. Phys. [5], **11**, 145.

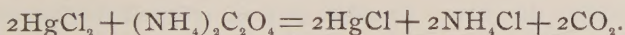
⁵ Ann. Chem. (Liebig), **249**, 137.

Under the class of polymerization come the facts discovered by Lemoin.¹ He found that chloral and styrolene are polymerized when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry as in the case of phosphorus and sulphur. The yellow phosphorus is converted into the red modification and a solution of sulphur in carbon bisulphide deposits the insoluble modification.

The work of Tyndall² on light reactions cannot be placed under any of these heads as the nature of the reaction is not known. He exposed the vapor of amyl nitrite to a beam of light and found that there was decomposition; oxides of nitrogen were formed but the other products were not examined. Tyndall also found that allyl iodide and isopropyl iodide are affected by light, but he did not study the subject from its chemical side.

Oxalic acid has been extensively used in photochemical reactions, especially in form of its salts, and it has been recommended as a means of determining the amount of sunlight. Döbereiner³ proposed to use ferric oxalate as a photometer in which the ferrous oxalate or the carbon dioxide given off could be measured. He also found that oxalic acid will reduce platinum chloride to metal and that silver oxalate is partially reduced to metal.

Eder⁴ used as a photometer solutions of ammonium oxalate and mercuric chloride which on exposure to sunlight gives off carbon dioxide and deposits mercurous chloride according to the equation,



Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which involve the use of uranium salts will be given in detail. The first person to find that uranium salts are sensitive to light was Bucholz,⁵ who described, in 1805, certain effects produced by the sulphate and alcohol. He says: Uranium sulphate dissolves in 25 parts of alcohol and the solution undergoes remarkable changes on exposure to the sunlight; the yellow

¹ Comp. Rend., **93**, 514.

³ Schweigger's Jour., **62**, 90.

⁵ Ann. Chim. Phys. [1], **56**, 142.

² Proc. Roy. Soc., **17**, 92, 104.

⁴ Wien. Academy Ber., **2**, 1879.

liquid becomes turbid and deposits a grayish green substance. After several days exposure the solution acquires an odor of nitric ether; the filtrate is colorless and contains no uranium; the precipitate is of a green color and retains sulphuric acid. Bucholz further observed that an ether solution of uranyl nitrate becomes green on exposure to sunlight and a black substance is deposited.

Chemists added little to these results until Ebelman,¹ in 1831, took up the subject. He confirmed the results of Bucholz with the uranium sulphate and alcohol, but noticed in addition that green crystals were formed which he said were the uranium protoxide. The precipitate he called the bi-basic sulphate of the protoxide and gave it the formula $2\text{UO}.\text{SO}_3 + 2\text{H}_2\text{O}$.

The uranium oxalate was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposed into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Corvissart,² working on the action of light on organic substances, noticed that if a solution of oxalic acid be exposed to the light it will quickly reduce a gold solution. They heated to boiling a four per cent. solution of oxalic acid with a one per cent. solution of uranyl nitrate, finding that in the dark no decomposition would take place, but after exposing to the sunlight action soon began. They say that carbon monoxide was given off, but do not mention having obtained any carbon dioxide. Another fact of interest discovered by them was that a small quantity of uranyl nitrate increased ten fold the action of light on any amylaceous matter, converting it into dextrin and glucose.

Seekamp³ repeated the work of St. Victor and Corvissart and found that after a solution of uranyl nitrate and oxalic acid had been exposed to the light for some time there was a deposit of a green crystalline powder, the solution became colorless and reacted acid. The acid was identified as formic acid by means of its lead and barium salts. From succinic

¹ Ann. chem. (Liebig), **43**, 294.

² Comp. Rend., **21**, —; Ann. chem. (Liebig), **43**, 114.

³ Ann. chem. (Liebig), **122**, 113.

acid he obtained carbon dioxide and propionic acid and the precipitate which was formed, he believed, to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyrotartaric acid.

H. C. Bolton,¹ in a review of the work done on uranium salts in photochemical reactions, adds some interesting facts discovered while working with certain uranium salts in photographic processes. He obtained a salt which is the double oxy-fluoride of uranium and potassium having the composition represented by the formula $2\text{UO}_2\text{F} + 3\text{KF}$. A solution of this salt acidified with formic acid decomposes in the sunlight, forming a precipitate which gives the formula $4\text{UF} + \text{KF}$. Oxalic acid causes a similar reduction but with the formation of Ebelman's violet hydrate. Solutions of the nitrate, sulphate, oxychloride, and oxyfluoride are reduced when mixed with glycerine and placed in the sunlight. Even in the dry state the uranium ammonium citrate was found to be sensitive to light.

Wisbar² next took up the study of light on uranium salts. He verified Seekamp's work on pyrotartaric acid and showed in addition that butyric acid in presence of uranium salts breaks down into propane and carbon dioxide.

Somewhat similar to the work of Wisbar is that of Louis Lucien Bonaparte,³ who obtained a decomposition of valeric acid by exposing it with a solution of uranyl valerate. The products formed he believed to be uranous valerate and gases which he believed to be carbon dioxide, carbon monoxide, and a hydrocarbon.

Chastaing⁴ studied the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol and noticed the odor of aldehyde which is probably the odor Bucholz took for *nitric ether*. Some uranyl acetate was formed in the solution.

At the suggestion of Prof. Remsen, H. C. Jones, working in this laboratory, undertook the study of the action of light on oxalic acid in the presence of uranium salts. As his work has not been published, a short account of the results which he obtained will be given.

¹ Amer. J. Sci. [2], **48**, 206.

³ Jour. für Prak. Chem., **30**, 308.

² Ann. Chem. (Liebig), **262**, 232.

⁴ Ann. Chim. Phys. [5], **11**, 145.

He verified the statement of Seekamp that, in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide and formic acid. The equation given by Seekamp to express the reaction, is



Seekamp¹ thought that the green compound precipitate was uranous oxalate, of the composition $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$.

A series of experiments was made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used. The amount of carbon dioxide found in every case agreed to within a few cubic centimeters with the amount of carbon dioxide which would have been liberated from the oxalic acid used, had it decomposed directly into carbon dioxide, carbon monoxide, and water. The amount of carbon monoxide set free, plus the amount combined as formic acid, was always somewhat less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate, relative to the free oxalic acid originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass.

Analyses of the precipitate formed, from various mixtures, confirmed the belief that the precipitate was a mixture. When a solution containing three grams of uranyl oxalate and thirty grams of oxalic acid had been exposed to the light for a time it was noticed that green crystals were forming on the bottom and sides of the flask. The solution was then removed from the direct sunlight and allowed to stand in diffused light for some time, when a considerable quantity of the crystals was obtained free from impurities. An analysis of the crystals dried between filter-paper gave uranium = 45.05 per cent., which agreed fairly well with the composition $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$, which contains 45.8 per cent. of uranium, on the basis $\text{U} = 240$, $\text{C} = 12$, $\text{O} = 16$.

Finally, a solution was prepared containing 3 grams uranyl oxalate and 45 grams oxalic acid. Pure crystals were ob-

¹ Seekamp, *Ann. chem. (Liebig)*, 122, 115.

tained, as described above, which contained 46.05 per cent. of uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that by using a large amount of uranyl oxalate, relative to oxalic acid, that the amorphous compound might be obtained in pure condition. For this purpose a solution containing 2 grams of uranyl oxalate and 2 grams of oxalic acid was exposed to the light. A greenish mass was at first precipitated, which, on longer exposure, became purplish-brown. A solution of uranyl oxalate exposed alone to the direct sunlight, apparently underwent the same transformation.

It was found further, that a very small amount of uranyl oxalate will decompose a very large, if not an unlimited amount of free oxalic acid, if exposed *continuously* to the direct sunlight. If not continuously, the crystalline compound will separate out of the solution and the action will cease. Thus the reaction suggested by Seekamp, and given above, cannot express the whole truth, since, in terms of it, one molecule of uranyl oxalate can decompose only two molecules of free oxalic acid.

The uranyl salt seems to act in some way as an oxidizing agent, as is indicated by the fact that the product precipitated is some reduction product of the uranyl compound originally used.

Decomposition of Oxalic Acid in the Presence of Uranyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of uranyl oxalate was not thoroughly settled by Jones, it was decided, at Prof. Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose, solutions containing oxalic acid and uranyl oxalate, in varying proportions, were exposed to the direct sunlight, and in all cases it was found that after considerable gas had been given off the solution became cloudy, and then deposited a light green crystalline powder. When all of the oxalic acid was decomposed, and the evolution

of gas had ceased, there was deposited the remainder of the uranium in solution as a flocky, purplish-brown substance. Evidently, concordant results could not be obtained by working with the precipitate as a whole, and it was decided to remove the light green colored precipitate when first formed.

To obtain it 3 grams uranyl oxalate and 2 grams oxalic acid were dissolved in a liter of water and exposed to the direct sunlight. When some of the green precipitate first formed had settled to the bottom of the flask it was filtered off, washed with water, and then dried between filter-papers. The dry substance has a very pale green color and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide U_3O_8 . In all of the analyses made this method was used; very often, however, the oxide formed was converted into the nitrate and the nitrate again decomposed. This was done simply to control the results, as the oxide U_3O_8 is more readily formed from the nitrate than from the uranium salt of organic acids.

In the green colored substance these results were obtained:

I. 0.2637 gram substance gave 0.1776 gram $U_3O_8 = 57.17$ per cent. U.

II. 0.2015 gram substance gave 0.1369 gram $U_3O_8 = 57.68$ per cent. U.

III. 0.2560 gram substance gave 0.1725 gram $U_3O_8 = 57.20$ per cent. U.

Calculated for $U(C_2O_4)_2$, 57.69 per cent. U.

This shows the substance to be uranous oxalate. It can be obtained at any time, provided the solutions be continuously exposed to the sunlight, and not too large an excess of oxalic acid be present. It was shown by Jones that when a large excess of oxalic acid is present, and the solution removed, after a short exposure to the light, there is a strong tendency to the formation of the crystalline product $U(C_2O_4)_2 \cdot 6H_2O$. If the solutions are exposed until all of the oxalic acid is decomposed there is then formed some of the purplish-brown substance.

Desiring to obtain the purplish-brown precipitate in pure condition, several attempts were made to get it from solutions

containing oxalic acid and uranyl oxalate by removing the uranous oxalate formed and subsequent exposure, but in all cases the precipitate contained a mixture of the two precipitates. When uranyl oxalate in solution is exposed to the sunlight, there is formed the same purplish-brown precipitate, and it was decided to use the uranyl oxalate alone for obtaining it.

Decomposition of Uranyl Oxalate.

Four grams of uranyl oxalate were dissolved in a liter of water and the solution filtered to get rid of a small amount of undissolved substance. The solution was exposed to direct sunlight, and within five minutes after exposure the clear yellow solution had become cloudy. The cloudiness increased rapidly. In half an hour there was a deposit of the purplish-brown substance on the bottom and side of the flask nearest the source of light. There was no evolution of gas whatever.

Thinking possibly the solution may have held the gas, several attempts were made to collect any gas formed by attaching large tubes filled with uranyl oxalate solutions to nitrometers containing mercury. Under much reduced pressure, and even by gentle heating, it was impossible to collect any gas. The precipitate formed in the above solutions was filtered off, washed with water, and left to dry in the air. The brown substance on drying changed to a yellow one, so that it was impossible to prepare it in this way for analysis. Even on drying rapidly between filter-papers there was some change noticed. If the brown substance be allowed to stand in the flask in which it is precipitated the same change takes place, although not so rapidly. The filtrate was always neutral to litmus and contained nothing except traces of uranium salts which were thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely, although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

Determination of Uranium in the Brown Precipitate.

Some of the freshly prepared substance was partially dried between filter-papers, transferred to a porcelain boat, and then

dried at 100° in a stream of dry hydrogen. The substance, prepared in this way, has a pale, grayish-green color, resembling somewhat uranous oxalate, and in this condition shows very little tendency to pass over into the yellow substance. It was weighed rapidly, placed in a combustion tube and heated in a current of oxygen. When heated under these conditions the substance begins to glow and the combustion spreads rapidly throughout the mass. After very few minutes the substance is changed into the oxide U_3O_8 . The boat was then withdrawn and weighed. The oxide obtained in this way is of a pale olive-green color, and appeared to be perfectly pure. The uranium was determined in six separate specimens in this way.

I.	0.4768	gram	gave	0.4407	gram	U_3O_8	=	78.47	per cent.	U.
II.	0.2373	"	"	0.2180	"	"	=	77.99	"	"
III.	0.1372	"	"	0.1249	"	"	=	78.00	"	"
IV.	0.1556	"	"	0.1414	"	"	=	77.15	"	"
V.	0.1856	"	"	0.1696	"	"	=	77.58	"	"
VI.	0.1454	"	"	0.1314	"	"	=	77.41	"	"

Average for the six determinations, 77.76 per cent. U.

These results, it will be seen, are fairly concordant, but good results could not be obtained for carbon.

Several attempts were made to determine the percentage of carbon, but the amount is so small in comparison with the large amount of uranium that concordant results could not be obtained. The substance, when heated alone, gives off small amounts of carbon monoxide, but even by passing the gases over glowing copper oxide, good results were not obtained. Better results were obtained with the yellow substance, into which the brown one passes on standing. These will be spoken of later. Various attempts were made to isolate the acid contained in this salt, but without success. The substance dissolves readily in hydrochloric, sulphuric, and nitric acids, forming green solutions, from which ammonia precipitates the black uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction product of uranyl oxalate. There can be no doubt that it contains a small percentage of carbon, as will be made more evident when the yel-

low transformation product is considered. Ebelman believed it to be a hydrated oxide, but the presence of carbon proves this assumption to be wrong. Bolton obtained the same precipitate by exposing a solution of the double oxyfluoride of uranium and potassium acidified with oxalic acid. He however did not analyze the product. If this were the simple hydrated oxide, it seems that it should also be formed with other acids than oxalic acid, especially when the same salt of Bolton is acidified with formic acid. In this case only the salt $4UF + KF$ is formed.

Analysis of the Yellow Substance Obtained from the Purplish-brown Precipitate.

The best way of preparing the yellow salt is to allow the brown substance to stand in a desiccator for four or five days. It is also formed when allowed to stand in the air, but it is more convenient to use the desiccator, as in this way the yellow salt can be obtained in dry condition having constant weight. For the analyses of this salt, it was dried to constant weight over sulphuric acid or by heating in an air-bath to 100° . The substance is also formed when the brown precipitate is allowed to stand under water for several weeks. A preliminary test was made for carbon by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution. There was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion tube as in the previous case, and the uranium oxide weighed afterward, thus determining the uranium, carbon, and hydrogen in the same operation. The substance was first converted into a brick-red substance, probably U_2O_3 , and on higher heating gave the oxide U_3O_8 .

Different preparations gave the following results on analysis:

	U.	C.	H ₂ O.
I.	75.46 per cent.	1.36 per cent.	8.58 per cent.
II.	75.40 " "	1.02 " "	8.04 " "
III.	75.10 " "	1.2 " "	8.50 " "
IV.	74.9 " "	1.15 " "	8.7 " "
V.	75.44 " "		

These results are selected from a much larger number of

analyses, all of which agree very closely with the ones given.

It is difficult to account for the small amount of carbon present, but as none of the carbon was given off in the original decomposition, and the brown substance does not lose any carbon dioxide in drying, it is safe to say that all the carbon is in combination with the uranium. In what form it exists it is difficult to say, as the substance dissolves in acids without separation of any organic acid. If all the uranium be precipitated and the filtrate separated, there is no evidence of any organic substance remaining behind.

*Formation of Formic Acid in the Decomposition of
Oxalic Acid.*

Jones has shown in his work that the equation of Seekamp, representing the decomposition of oxalic acid by uranyl oxalate, does not express the reaction, as it does not account for the formic acid formed nor for the carbon monoxide. It was thought advisable to make a few experiments to see whether formic acid can be built up from carbon monoxide and water in presence of uranium salts. For this purpose the following experiments were made:

I. A 250 cc. Erlenmeyer flask was filled with uranyl oxalate solution, and then there was collected in it about 100 cc. carbon monoxide. The inverted flask was connected with a long tube bent twice at right angles to denote the pressure. The flask was exposed to the direct sunlight. Within two hours the decomposition of the uranyl oxalate had ended. The precipitate was the same as the one spoken of above when uranyl oxalate decomposes. No free acid was detected in the solution.

II. Carbon monoxide and water were exposed for fifteen days to the direct sunlight. On examination, at the end of this time, the water was perfectly neutral.

III. Mixtures of equal values of carbon monoxide and carbon dioxide, in the presence of water, were exposed to the direct sunlight, but without obtaining any formic acid.

From these experiments it is shown that the formic acid formed in the decomposition of oxalic acid is from the oxalic acid itself and not from the combination of carbon monoxide and water.

Decomposition of Malonic Acid.

The study of malonic acid was next taken up and it was our purpose to proceed as in the case of oxalic acid, but unexpected difficulties arose.

Uranyl malonate was prepared by bringing together hot concentrated solutions of malonic acid and uranyl nitrate. It separates in a few moments as a bright yellow crystalline powder, adhering firmly to the sides of the beaker. It is nearly insoluble in water and alcohol, more readily soluble in nitric acid and easily soluble in a solution of malonic acid.

On analysis it gave the following results for uranium:

Calculated for $\text{CH}_2\left\langle\begin{smallmatrix}\text{COO} \\ \text{COO}\end{smallmatrix}\right\rangle(\text{UO}_2)\cdot 3\text{H}_2\text{O}$, 56.06 per cent.

0.2526 gram gave 0.1656 gram $\text{U}_3\text{O}_8 = 55.65$ per cent. U.

0.3682 " " 0.2416 " " = 55.70 " " U.

Heated to 110° for 3 hours it lost 9.15 per cent. H_2O .

Calculated for $2\text{H}_2\text{O}$, 8.78.

At 180° , 0.2670 gram lost in weight 0.0325 gram = 12.16 per cent. H_2O .

Calculated for $3\text{H}_2\text{O}$, 12.6 per cent. H_2O .

This, like many uranium salts, loses some water readily, but loses the last molecule only at high temperatures.

As this salt is almost insoluble in water it could not be used for any decompositions. Accordingly, dilute solutions of uranyl nitrate and malonic acid were exposed to the light, but within a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate and it was hoped to use such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranium malonate in the required amount of potassium malonate. On evaporation, well-formed but small, very bright yellow crystals were obtained.

Solutions of this salt, with and without free malonic acid, were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the brightest sunlight.

The same results were obtained when the uranyl malonate was dissolved in malonic acid and exposure made of the solution. The malonic acid decomposes when a dilute solution of

uranyl oxalate and malonic acid is exposed to the sunlight, but the rate of decomposition is so extremely slow that it was not considered advisable at the time to carry the work further.

Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid by means of the uranyl succinate, but so far it has been impossible to effect such a decomposition.

Uranyl succinate is described in Watt's Dictionary as being made from uranyl nitrate and acid sodium succinate by evaporation to dryness. This method was tried, but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was dissolved in a dilute solution of succinic acid and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried to make the uranyl succinate, but they were not successful. Solutions of uranyl nitrate and succinic acid can be evaporated to crystallization when they crystallize separately. It was also hoped to get it from barium succinate and uranyl sulphate. These salts were brought together in molecular proportions, but part of the barium was changed into sulphate and part into the insoluble barium uranate.

As it was desired to obtain the decomposition of succinic acid by means of uranyl succinate the experiments were carried no further.

Seekamp¹ found that succinic acid decomposes in the sunlight in the presence of uranyl nitrate into carbon dioxide and propionic acid. This was verified qualitatively. The action takes place rather slowly and as this work could be carried on only during the winter and early spring months it was not carried further. Seekamp believed the green precipitate in this case to be uranous succinate. A small amount of this substance was obtained and analyzed for uranium, but the percentage did not agree with that required for uranous succinate.

It is necessary to do much more work on the precipitates obtained in these decompositions as they are difficult to ob-

¹ Ann. chem. (Liebig), 133, 253.

tain in pure state and from analyses made of precipitates from other acids they do not appear to be the simple reduction product.

Decomposition of Tartaric Acid.

When tartaric acid and uranyl nitrate are exposed to the sunlight, the clear yellow solution gradually turns to a deep green color and after a few hours there is a precipitation of a light green colored salt. No gas is given off in the reaction. Several solutions were attached to nitrometers containing mercury, but there was no change in the volume although the solutions were under much reduced pressure. Heat facilitates the precipitation very greatly. Some of the green solution from which the precipitate had been removed was placed on a water-bath when there was a complete precipitation in a few minutes. The most favorable conditions for obtaining the precipitate is when one molecule of uranyl nitrate is exposed with one molecule of tartaric acid. If the solution in which the precipitate has been formed be allowed to stand in the sunlight for several weeks, the green-colored salt goes into solution forming an amber-colored liquid.

For analysis the green colored salt was dried between filter paper and then over solid potassium hydroxide. It gave the following results:

I.

0.2631	gram	gave	0.1529	gram	U_3O_8
0.2631	"	"	0.0555	"	H_2O
0.2631	"	"	0.1396	"	CO_2

II.

0.2949	gram	gave	0.1713	gram	U_3O_8
0.2949	"	"	0.0684	"	H_2O
0.2949	"	"	0.1662	"	CO_2

Calculated for $U_6H_{12}O_{10}$.

	Per cent	I.	Found.	II.
Uranium.....	49.58	49.3		49.31
Hydrogen.....	2.48	2.34		2.57
Carbon	14.87	14.46		15.3

The nature of the above precipitate cannot be learned from the above results and the formula suggested has no signifi-

cance at present. It may be possible to isolate the organic portion of the salt, but until this has been done it would be useless to speculate in regard to the nature of the precipitate.

Decomposition of Isobutyric Acid.

Wisbar¹ has studied the action of sunlight on butyric acid in the presence of uranium salts and found that it decomposed into propane and carbon dioxide. It was thought desirable to know whether the other acids of this series underwent a similar decomposition and a study was made accordingly of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first as it was found to work readily, giving off gas freely when exposed to the sunlight with uranyl nitrate.

Experiments were first made to see whether any definite relation existed between the gases given off. Carbon dioxide was shown to be present by its ready absorption by potassium hydroxide and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame, showing it to be a hydrocarbon.

It was believed that the isobutyric acid would decompose in the same way as the butyric acid giving equal volumes of propane and carbon dioxide. This was found to be the case as is shown in the following experiments :

I. For the purpose of collecting the gases the solutions were exposed in small test tubes 12 × 120 mm. connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was weighed directly into the tube and a weighed portion of uranyl nitrate was added. Water was now added to bring the solution to the required height in the tubes.

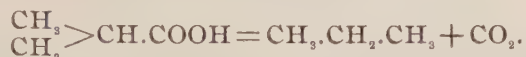
2.0201 grams isobutyric acid and 0.3364 gram uranyl nitrate were dissolved in 30 cc. water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy and there soon appear small drops of a dark green, viscous liquid, which gradually collects in the bottom of the test tube. Most of the gas

¹ Ann. chem. (Liebig), **262**, 232.

evolved seems to come from this large drop. This dark green heavy liquid is however not always formed and it depends on conditions which have not as yet been learned. There is always formed a precipitate however, either this liquid or a light green powder.

The exposure was continued for several days when all action ceased. All of the uranium was precipitated.

The total volume of gas was 30 cc. and of this 14.8 cc. were absorbed by caustic potash, which shows half the volume of gas to be carbon dioxide. This also shows that the total decomposition of the acid to have been approximately 30 per cent. of that calculated for the reaction,



At the end of the first day's exposure 21.5 per cent. of the decomposition had taken place.

II. This experiment went precisely as the preceding except that after the reaction had begun a tube filled with warm water was placed around the tube containing the solution. This increased the reaction very much and it was found by this method that large quantities of the gases can be collected in a very short time. Of 27 cc. of gas collected 13.6 cc. were absorbed by caustic potash.

III. In this experiment much larger quantities of acid and uranyl nitrate were used so as to collect a pure specimen of the hydrocarbon for analysis. After 25 cc. of the gas had been collected it was removed from the nitrometer so as to get rid of any gases, oxygen, or nitrogen, which may have been held in solution by the water used. This was repeated several times before a sample of the gas was collected for the analysis of the hydrocarbon.

The removal of the gas was made by having the gas under pressure by means of the pressure-tube connected with the nitrometer, and then opening the glass stop-cock of the nitrometer only a little way. The stop-cock was closed before all of the gas had escaped, thus making sure that no air could enter. By this means it was found possible to collect the evolved gases, so that, on absorption, exactly half of the volume

was shown to be carbon dioxide. The remaining portion was then transferred to a eudiometer and exploded with oxygen.

Volume of original gas	21.3 mm.	= 1 volume.
Volume after addition of oxygen	400.7 "	= 18.81 "
Volume after explosion.....	335.9 "	= 15.76 "
Contraction		= 3.05 "

The calculated contraction for C_3H_8 is three volumes. This proves the hydrocarbon to be propane, and the reaction is to be represented by the equation,



Decomposition of Propionic Acid.

Uranyl nitrate and propionic acid, when exposed to sunlight, decompose very readily, giving off gas in a few minutes after exposure is made. It was found best to use a rather strong solution of the acid. The gas is given off evenly and continues until nearly all of the acid is decomposed. The gas was collected and analyzed in the same manner as described under isobutyric acid.

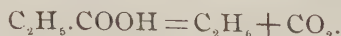
I.	32.4 cc. of gas gave.....	15.8 cc. CO_2 .
II.	30.5 " " " "	15.1 " "
III.	26.7 " " " "	13.2 " "

These figures show that approximately half the volume of the gas is carbon dioxide.

The residual portion was run into a eudiometer and exploded with oxygen.

Volume of original gas.....	19.97 mm.	= 1 volume.
Volume after addition of oxygen	201.12 "	= 10.07 "
Volume after explosion.....	147.44 "	= 7.38 "
Contraction		2.69 "
Calculated contraction for C_2H_6		2.5 "

This shows the hydrocarbon to be ethane and the decomposition of propionic acid is to be represented by the equation,



Decomposition of Acetic Acid.

Various attempts were made to decompose acetic acid in the

same manner as propionic, and isobutyric acid, but it was decomposed only with difficulty. The only proportions which were found to give off gas was when 15 cc. glacial acetic acid and 5 cc. strong solution of uranyl acetate were exposed. From this solution gas was given off, but only extremely slowly. The exposure was made in April and May, taking about six weeks to collect enough for analysis. The clear yellow solution did not change to the green color, so characteristic in all the other cases, to any extent. There was a slight green color, but it was not marked.

Analysis of gas—

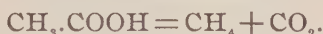
13.4 cc. of gas gave 6.4 cc. CO_2 .

Volume of original gas..... 13.2 mm.=1 volume.

Volume after addition of oxygen.. 108.24 " =8.2 "

Volume after explosion 80.52 " =6.1 "

Calculated contraction for CH_4 is two volumes, while that found is 2.1 volumes, which shows the gas to be methane, and the decomposition is to be represented by the equation,



It is interesting to note that the power of decomposition ceases with acetic acid, which breaks down under the influence of light only with difficulty. The power is apparently lost in formic acid, as it has been impossible so far to affect any decomposition of this acid by light in the presence of uranium salts.

Comparison of the Rates of Decomposition of Propionic, Butyric, and Isobutyric Acids.

For the purpose of comparing the relative rate of decomposition of these three acids, tenth normal solutions were made of each and varying amounts of the acid were exposed with varying amounts of uranyl nitrate. It was decided to use propionic acid as the standard in determining the best conditions possible. The following table shows the comparison between two solutions of propionic acid exposed under exactly similar conditions.

No. of days.	Hours of exposure.	Amount of gas collected.		Condition of weather.
		No. 1.	No. 2.	
1.	2	0.8	0.6	Clear.
2.	7 $\frac{1}{2}$	2.8	2.8	"
3.	7 $\frac{1}{2}$	3.4	4.0	"
4.	7 $\frac{1}{2}$	4.0	7.2	"
5.	15	4.3	9.2	"

Solution No. 1 contained 10 cc. of one-tenth normal $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 10 cc. one-tenth normal propionic acid.

Solution No. 2 contained 15 cc. one-tenth normal propionic acid and 5 cc. one-tenth normal $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The comparison is not exactly fair, as the precipitate which is formed some time after the decomposition begins has some effect, as will be seen in the following table, in which is given a comparison of propionic, butyric, and isobutyric acids. Each solution contains 15 cc. one-tenth normal acid and 5 cc. one-tenth normal $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

No. of days.	Amount of gas collected.		
	Propionic.	Isobutyric.	Butyric.
1.	1.2	1.4	1.0
2.	2.5	3.0	2.5
3.	4.0	4.7	3.6
4.	5.3	5.7	4.3
5.	5.3	5.7	4.3
6.	6.5	6.4	4.9
10.	7.6	7.4	5.8
11.	8.8	8.4	...
12.	10.2	9.5	...
13.	12.0	10.6	9.0
14.	13.6	11.4	9.6
15.	15.0	12.4	10.5
16.	15.8	12.8	11.2
17.	16.3	13.0	11.2

It will be seen that on the sixth day the amount of gas collected from the propionic acid and the isobutyric acid is practically the same. Up to this time there was only slight cloudiness in the solutions, but after three days of rain there was found a precipitate in the solution containing isobutyric acid. From this time on it will be seen that there is a gradual gain

in the amount of gas collected from the propionic acid over the amount collected from the isobutyric acid.

As the weather was unfavorable for carrying these comparisons any further, the subject was dropped at this point, but it is believed that interesting comparisons can be obtained by working during the summer months.

SUMMARY.

It has been shown that the precipitate in the solutions of uranyl oxalate and oxalic acid is formed in two stages: (1) formation of uranous oxalate, (2) formation of the purplish-brown precipitate from the uranyl oxalate left in solution. The nature of the latter has not been cleared up, but it is shown to contain carbon, and consequently cannot be the hydrated oxide as supposed. The formic acid found when oxalic acid is decomposed must come from the oxalic acid itself, as all attempts to build it up from water and carbon monoxide in presence of uranium salts, has failed.

Tartaric acid, when exposed with uranium salts to the sunlight, forms an insoluble precipitate with uranium, the nature of which has not been cleared up.

It has finally been shown that acetic, propionic, and isobutyric acids, decompose into the hydrocarbons corresponding to the acids and into carbon dioxide.

BIOGRAPHICAL.

The author was born at Williamsburg, Penna., January 12, 1868. His early education was received in the public and private schools of Altoona, Penna. In 1885 he entered Lafayette College and received the degree of Bachelor of Arts in 1889, and the degree of Master of Arts in 1892. He went to the Johns Hopkins University in October, 1890. In February, 1893, he left to accept a position in the laboratory of the Pennsylvania Railroad Company, but returned in October of the same year. He was appointed lecture assistant to Professor Remsen in 1893, which position he has held for two years.

